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PHYSICAL METALLURGY OF BETA TITANIUM ALLOYS.(U)
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UNCLASSIFIED ABSTRACT (cont.)

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↙ of adding Al and Si to beta alloys indicates that yield stress and Young's modulus are increased while density and ductility are decreased. It appears that Al increases the ductile brittle transition temperature. ↗

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1. Research Objective

The goal of this investigation has been to obtain an understanding of phase equilibria and the interrelationship of microstructure and properties in fully stabilized β -Ti solid solutions strengthened by precipitation of intermetallic compounds such as Ti_5Si_3 , Ti_5Ge_3 and TiAl . This understanding is necessary to provide a basis of assessing the potential of such alloys as low density substitutes for nickel alloy disks and blades in the high temperature stages of compressors in gas turbine engines. Minimum acceptable properties for this application are yield stress = 75 ksi, total, elongation = 10 pct, stress for 0.2 pct creep in 1000 hrs = 42 ksi and $(\dot{E}/\rho)^{1/2} = 8800 \text{ in}^{1/2}$ at the operating temperature. A candidate alloy should be forgable, deep hardening and oxidation (flame) resistant.

Specific objectives of this investigation have been to determine (i) the stability limits and physical properties of β -Ti solid solutions with additions of Mo, V, Cr and Al. (ii) the effect of precipitation of Ti_5Si_3 and Ti_5Ge_3 on the mechanical properties of β -Ti solid solutions. (iii) the phase boundaries of the β -TiAl phase field and the physical properties of β -TiAl alloys.

2. Results

Tarek Khaled completed his dissertation¹ titled "Phase equilibria in Beta Titanium Alloys". In his research, which was supported entirely by this grant, he investigated phase equilibria in the Ti-(V,Mo,Cr) system with Cr additions up to

10 wt pct and determined the β -transus, i.e., the α ($\alpha+\beta$) phase boundary, in the Ti-V, Ti-Mo, Ti-V-Mo and Ti-V-Mo-8 wt pct Cr systems at and below 600°C. Three papers have been written based on Khaled's research.²⁻⁴ References 2 and 3 are included in Appendices A and B, respectively.

From the standpoint of assessing the potential of β -Ti alloys for application in compressors in gas turbine engines, Khaled's results identify composition ranges where the equilibrium phase is β as-cast alloys can be cold rolled and loss of ductility during heat treatment is minimal. More specifically, his results indicate: V and Mo are the most effective stabilizers; chromium, if present in amounts exceeding several per cent, enhances oxygen segregation to grain boundaries causing precipitation of α or oxide phases; and, the Mo content should be limited to a maximum of 15 wt pct to avoid the precipitation of embrittling oxide phases during heat treatment.

Norman Elfer's dissertation research has been concerned with improving the properties of β solid solutions. He determined the modulus and density of various Ti-V-Mo-Cr solid solutions.⁵ Further, he has studied the effect of Al and Si additions on modulus and density. Extrapolating his results, it appears that the $(E/\rho)^{1/2}$ value of a β -alloy may be made to exceed 8800 in^{1/2} at temperatures greater than 1000°F, see Fig. 1. Elfer also found that the maximum solubility of Si in β -Ti at 1000°C, a convenient solutionizing temperature, is between 0.4 and 0.7 wt pct.

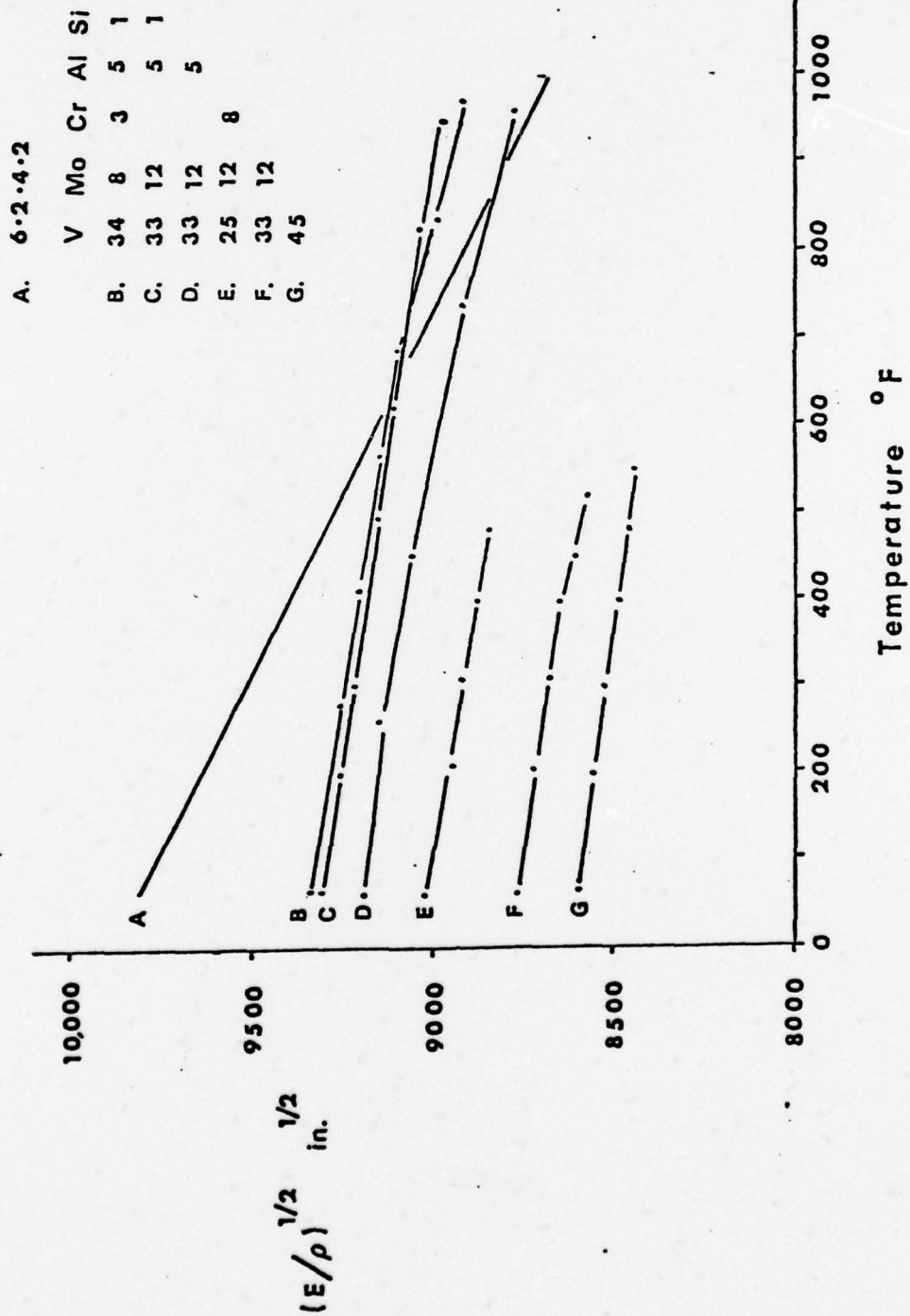
On the basis of these findings an alloy composition was

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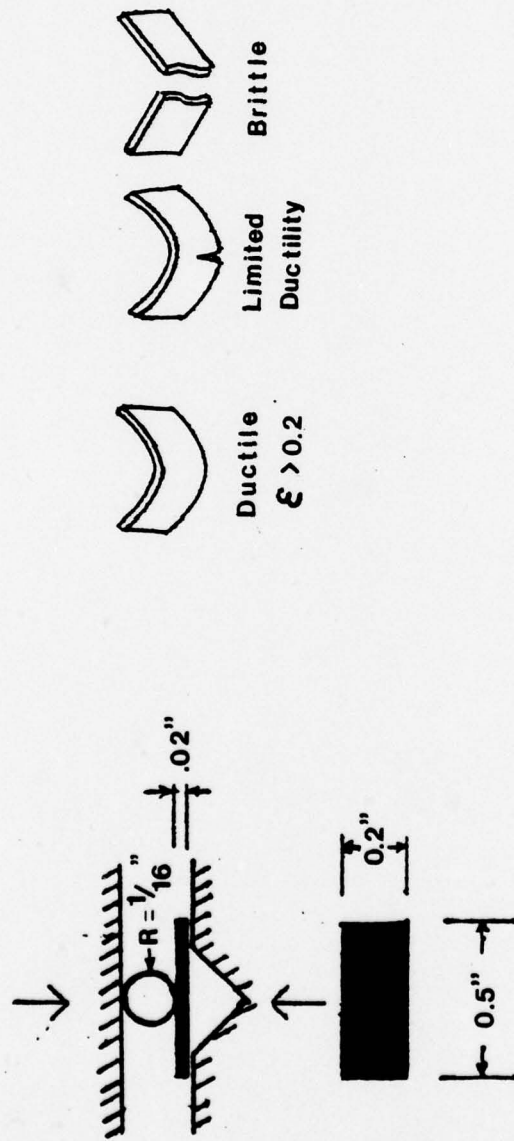
Modulus to density ratio to the one half power versus temperature for various beta alloys

Figure 1

selected for detailed study, namely, Ti-38V-12Mo-5Al-0.5 Si. Studies of this alloy cast as a 5 gm button indicated that it could be cold rolled and was a stable β alloy. Two ingots of this alloy were ordered from RMI of Niles, Ohio. Forging and hot rolling of these ingots caused cracking. Extrusion of these ingots was ordered in January 1978. The ingots were remelted to 3 inch diameter and canned in iron jackets. Extrusion was attempted at 1650, 1850 and 2000°F. At 1650 and 1850°F, their 364 ton press stalled. Thermal expansion at 2000°F made the ingots too large for the press. They were removed from the cans and coated with glass. Extrusion was attempted at 2000°F but again the press stalled. At this point the ingots were returned to USC.

Because of the difficulties with the RMI ingots, 40 gm buttons of the alloy were prepared with the idea of cold rolling them into sheet specimens. Surprisingly, it was found that while 5 gm buttons of the alloy could be cold rolled, into sheet, 50 gm buttons could not.

In order to investigate this surprising result, a 5 gm button of Ti-33V-12Mo-5Al was cold rolled to 0.020 in strip. Rectangular specimens were cut out and recrystallized at 1000°C for 1, 2, 3 and 4 hours giving grain sizes ranging from 0.10 to 0.29 mm. The results of bend tests on these specimens is shown in Fig. 2. A ductile brittle transitions was observed to occur at a temperature that increased with increasing grain size. Similar tests were carried out on specimens of Ti-33V-12Mo-2Al. Specimens with up to 0.29 mm grain size were ductile above -80°C.



Ductile Brittle Transition Temperature
versus Grain size for Ti-33V-12Mo-5Al Alloy

Figure 2

Tests on Ti-37V-8Cr-5Al gave similar results to Ti-33V-12Mo-5Al. Thus, it appears that adding Al raises the ductile brittle transition temperature of β alloys and that for a 5 wt pct Al addition the transition temperature can be greater than room temperature if the grain size is sufficiently large.

Employing energy dispersive x-ray analysis on the SEM, it was found that Mo concentration varied from the dendrite cores to the interdendritic regions by 2 wt pct in the 5 gm button. While in the 10 gm buttons it varied by 4 wt pct. Such differences in composition could easily produce regions in the 40 gm buttons with ductile brittle transitions above room temperature, thereby explaining their failure to cold roll.

In view of these observations, it was decided that despite the RMI experience hot working offered the most promising approach for obtaining test specimens of the Ti-38V-12Mo-5Al-0.5 Si alloy. Hot working should break up the cast structure and might, if the temperature and reduction ratio were chosen properly, give a small enough grain size to produce a ductile alloy at room temperature. Accordingly, Dr. Harris Burte of AFML was contacted regarding extrusion of the Ti-38V-12Mo-5Al-0.5 Si alloy with the AFML high thrust, high temperature press. He agreed and with the cooperation of Dr. Brick Adair the alloy was finally extruded. Also 18 40 gm buttons of this alloy and closely related alloys were sent to Dr. Tom O'Connell of the Government Products Division of Pratt and Whitney Aircraft, West Palm Beach, Florida, who had kindly agreed to isothermally forge them in the edgewise configuration.⁷ Finally, several

alloys containing less V, Mo and Al than the Ti-38V-12Mo-5Al-0.5Si alloy were cast moderate size buttons with the idea of rolling them into sheet and cutting out specimens. It was recognized that this alloy would not be a stable β Ti alloy but it was hoped the amount of α present would be small.

The extrusions obtained from AFML were sound. Unfortunately, the grain size fell in the range where limited ductility would be predicted at room temperature and indeed only limited ductility has been observed. The isothermal forgings from Pratt and Whitney Aircraft had a grain size sufficiently large that brittle behavior would be expected, and indeed brittle behavior was observed. Alloys with the following compositions were cast as moderate size buttons and cold rolled into sheet:

A Ti-28.5 V-9Mo-3.8 Al-0.5Si

B Ti-28.5 V-9Mo-3.8 Al

C Ti-25.8 V-9Mo-2.3Al

D Ti-25.8 V-9Mo-5.2Al

These alloys contained somewhat more α than was desired, Fig. 3. The tensile properties were, however determined and are given in Table 1. In addition to these results a creep test was carried out on alloy A after aging for 250 hours at 600°C. A time to failure of 22 hours was observed under a 50 ksi load at 1000°F. The strain at failure was 25%. Because of the discouraging results of the mechanical tests and lack of time oxidation and flammability experiments were not attempted on the alloys.

Earlier in the program, considerable effort was expended



Microstructure of Ti-28.5V-9Mo-3.8Al alloy solutionized for 15 minutes at 1000°C and aged for 250 hours at 600°C. A circular α is clearly visible in β matrix

Figure 3

Alloy	Heat Treatment	Temp (°C)	0.2%Y.S. (ksi)	T.S. (ksi)	ϵ_T (%)
A	15min/1000°C	R.T.	129	130	18
A	15min/1000°C +250 hours/610°C	R.T.	146	165	2.5
A	15min/1000°C	200	103	114	12
A	15min/1000°C	509	92	114	15
A	15min/1000°C	550	107	131	14
A	15min/1000°C +250hours/610°C	550	107	131	14
B	15min/1000°C	RT	125	125	12.5
C	"	RT	122	124	26
D	"	RT	118	115	19
A	1hour/1000°C	RT	95	95	19
B	"	RT	122	120	22
D	"	RT	127	125	16

Table 1 Tensile Testing Results

investigating a group of alloys consisting primarily of a two phase mixture of TiAl and β . The idea was to obtain a microstructure where TiAl was imbedded in a matrix of β which was assumed to have the greatest ductility. The alloys were arc melted as buttons and then isothermally forged by Tom O'Connell Government Products Division, Pratt and Whitney Aircraft, West Palm Beach. As previously reported, the alloys were found to be brittle, however, the origin of the brittleness was not established.⁵ On the basis of our more recent result, it appears likely that the equilibrium β phase present in these alloys contained enough Al, and the grain size of these alloys was sufficiently large that their ductile brittle transition temperature should have been well above room temperature.

During the course of this program, we have attempted to access the potential of β alloys as low density substitutes for nickel alloys in the high temperature stages of gas-turbine engines. At the time we began this program, concerns had been expressed regarding the high density, low modulus, high diffusivities and low oxidation resistance of this type of alloy.⁸ We have shown that by adding Al it is possible to prepare β solid solutions with $(E/\rho)^{1/2}$ greater than 8800 in^{1/2} in the range 1000-1100°F. Because of our recent discovery, however, that Al raises the ductile brittle transition temperature, it appears that the use of this element must be limited to about 2 pct. Thus, based on equations previously reported⁶ giving E and ρ for β -Ti alloys at room temperature (alloying additions in wt pct) $E(\text{psi} \times 10^{-6}) = 10.5 + 0.067V + 0.175\text{Mo} + 0.207\text{Cr} + 0.222\text{Al} + 0.130 \text{ Si}$

$$\frac{1}{\rho}(\text{in}^3/\text{lb}) = 6.15 - 0.016V - 0.034\text{Mo} - 0.023\text{Cr} + 0.041\text{Al} + 0.037\text{Si}$$

it would appear that a room temperature value of $9078 \text{ in}^{1/2}$, which would extrapolate to $8600 \text{ in}^{1/2}$ at 1000°F , would be more realistic. This could be achieved with a Ti-38V-12Mo-2Al-0.5Si alloy. In order to fabricate specimens for mechanical testing in this program, we reduced alloying additions to the point that a stable β alloy was no longer achieved. Consequently, the low creep resistance observed should not be taken as proof that the creep resistance of an all β matrix containing silicides would be low. While systematic oxidation experiments were not carried out, neither embrittlement nor excessive weight loss were observed in the high temperature tensile tests and creep test. Finally, it appears that the concept of stable β matrix strengthened by TiAl does not merit further effort. Due to the high Al content of the equilibrium β phase the ductile brittle transition temperature will probably exceed room temperature.

References

1. T. Khaled "Phase Equilibria in β -Ti Alloys" Ph.D. Dissertation, University of Southern California, June 1977.
2. T. Khaled, G. H. Narayanan and S. M. Copley, "Phase Equilibria and Interstitial Effects in the Ti-V-Mo System" Met. Trans. 9A, 1883-90 (1978).
3. T. Khaled, G. H. Narayanan and S. M. Copley, "Stability of the Beta Phase in the Ti-V-Mo-Cr System" accepted for publication in Met. Trans. (1979).
4. T. Khaled, G. H. Narayanan and S. M. Copley "The Effect of Interstitials on Phase Equilibria in $\rho(\text{Ti, Zr, Hf})$ - $x(\beta$ -stabilizers) Alloy Systems. This manuscript is being prepared for submission to Met. Trans.

5. S. M. Copley, Annual Technical Report 1976, AFOSR-75-2766, September 1976.
 6. S. M. Copley, Annual Technical Report 1977, AFOSR-75-2766, September 1977.
 7. S. M. Copley, Progress Report for No-Cost Extension of AFOSR-75-2766, September 1978.
 8. Harry W. Rosenberg, Chapter in Titanium Science and Technology R. I. Jaffee and H. M. Burte, Editors, Plenum Publishing Co., New York (1973).
-
3. Publications
 1. S. M. Copley and J. C. Williams, "High Strength Nonferrous Alloys," chapter in Alloy and Microstructural Design, ed. by J. K. Tien and G. S. Ansell, Academic Press, New York (1976).
 2. T. Khaled, "Phase Equilibria in β -Ti Alloys" Ph.D. Dissertation, University of Southern California, June, 1977.
 3. T. Khaled, G. H. Narayanan and S. M. Copley, "Phase Equilibria and Interstitial Effects in the Ti-V-Mo System" Met. Trans 9A, 1883-90 (1978).
 4. T. Khaled, G. H. Narayanan and S. M. Copley "Stability of the Beta Phase in the Ti-V-Mo-Cr System" accepted for publication in Met. Trans. (1979).
 5. T. Khaled, G. H. Narayanan and S. M. Copley, "The Effect of Interstitials on Phase Equilibria in $\rho(\text{Ti,Zr,Hf})$ - $x(\beta$ -stabilizers) Alloy System. This manuscript is being prepared for submission to Met. Trans.
 6. N. Elfer, Ph.D. Dissertation, University of Southern California, July 1979.
 7. N. Elfer, G. H. Narayanan and S. M. Copley, "The Effect of Al and Si on the Properties of Beta Titanium Alloys" to be submitted to Met. Trans.

4. Personnel

Principal Investigator

Stephen M. Copley - Kenneth T. Norris Professor of Metallurgical Engineering, Professor of Materials Science and Mechanical Engineering, Chairman, Department of Materials Science

Senior Investigator

G. Hari Narayanan - Assistant Professor of Materials Science and Mechanical Engineering
Professor Narayanan left USC during Summer 1978 and is now Metallurgist, Boeing Co. Seattle, Washington State

S. L. Narasimhan - Senior Research Associate
Dr. Narasimhan left USC during Summer 1977 and is now Engineering Supervisor, Research and Development, Eaton Corp. Battle Creek, Michigan.

Norman Elfer - Research Assistant
Norman Elfer should complete work on his Ph.D. dissertation in July 1979. He has accepted an appointment as Assistant Professor at Louisiana State University, Baton Rouge, Louisiana.

Tarek Khaled - Tarek Khaled completed work on his Ph.D. dissertation in June 1977 and is now Research and Development Materials Engineer, Ford Aerospace and Communication Corp. Newport Beach, California.

Virendra Rana - Virendra Rana contributed briefly to and was supported by this program. He completed his Ph.D. dissertation in 1977 and is currently Research Scientist, Bell Telephone Research Laboratories, Murray Hill, New Jersey.

5. Interactions

5.1 Conference Presentations

1. S. M. Copley and J. C. Williams, "Alloy Design for Strength (Non-Ferrous), MATCON '74, Detroit, Michigan, October 1974.
2. G. H. Narayanan, S. L. Narasimhan and S. M. Copley, "Microstructure and Mechanical Properties of Beta Ti-V-Al Alloys Containing TiAl(γ) Precipitates. Materials Science Symposium, November 11-13, 1975, Cincinnati, Ohio.
3. G. H. Narayanan, T. Khaled, S. L. Narasimhan and S. M. Copley, "Fully Stabilized Beta-Titanium Alloys," WESTEC '76 ASM/SME, Los Angeles, California, March 8-11, 1976.
4. T. Khaled, G. H. Narayanan and S. M. Copley, "Phase Equilibria in Ti-V-Mo System," WESTEC '76 - ASM/SME, Los Angeles, California, March 8-11, 1976.
5. S. M. Copley, "Beta Titanium Alloys for High Temperature Applications" Golden Gate Welding and Metals Conference." San Francisco, California, January 26-28, 1977.
6. N. Elfer, G. H. Narayanan and S. M. Copley, "Precipitation Hardened Beta Titanium Alloys", WESTEC '77, Los Angeles, California March 14-17, 1977.

5.2 Coupling

- | | |
|------------|--|
| March 1975 | Telephone discussion with Jim Hall (AFML) of research program: S. M. Copley (USC). |
| March 1975 | Visit to USC by A. Rosenstein (AFOSR). |
| May 1975 | Discussion of research program at Spring Meeting TMS-AIME, University of Toronto. G. Hari Narayanan (USC) and M. J. Blackburn (P&WA); G. Nari Narayanan & D. Koss, Michigan Tech. |
| Nov. 1975 | S. M. Copley and S. L. Narasimhan participated in an AFOSR/AFML Working Group Meeting at the University of Cincinnati. |
| Nov. 1975 | S. M. Copley discussed objectives and progress in this program with Martin Blackburn, Pratt and Whitney Aircraft; Jim Hall, AFML; Karl Brösius, TIMET and Shiro Fugishiro, AFML at 1975 Materials Symposium, Cincinnati, Ohio. |
| Nov. 1975 | S. L. Narasimhan visited with H. A. Lipsitt at AFML on November 14 and discussed the β - γ alloys. |

February 1976 S. L. Narasimhan arranged with the help of H. A. Lipsitt, AFML and T. O'Connell, Pratt and Whitney Aircraft, West Palm Beach, Florida, to have six γ - β alloys hot forged at 1200°C at the West Palm Beach facility. Alloys were sent on February 2, 1976.

February 1976 S.L.M. Sastry presented a seminar at USC on February 27, 1976 titled "High Temperature Titanium

We received hot forged β - γ alloys from P&WA, Florida on March 1, 1976

A. Rosenstein, AFOSR, visited USC to discuss this program on March 4, 1976.

S.M. Copley discussed by telephone the possibility of including a β -type alloy in a future AFML evaluation program on high temperature titanium alloys with Major W. B. Crow, AFML, March 1976.

S. M. Copley discussed with M. Fine Northwestern University, the selection of alloys for an investigation by Dr. Fine as a part of his AFOSR sponsored program. Dr. Fine visited USC in April 1976.

S. M. Copley corresponded with H. A. Lipsitt, L. Bidwell, AFML, regarding the application of alloys developed in this program in compressors.

S. M. Copley to H. A. Lipsitt, 12/23/76

S. M. Copley to L. Bidwell, 12/23/76

H. A. Lipsitt to S. M. Copley, 1/5/77

S. M. Copley discussed the applications of alloys developed in this program in compressors with M. Blackburn, Commercial Products Division, United Technologies Corporation, January, 1977.

S. M. Copley discussed the results of this program Jim Hall, TIMET, at Quintech 77, January, 1977.

S. M. Copley discussed the possibility of powder metallurgy approaches to forming beta titanium alloys with H. A. Lipsitt at Rapid Solidification Conference, Reston, VA., November, 1977.

S. M. Copley discussed results of this program Jim Williams and Martin Blackburn at Annual AIME Meeting, New Orleans, February 1979.

S. M. Copley and N. Elfer discussed various aspects of fabricating beta titanium alloys with Dr. Brick Adair, AFML on several occasions between, September 1978 and March 1979.

S. M. Copley and N. Elfer discussed various aspects of fabricating beta titanium alloys with Tom O'Connel (Government Products Division, Pratt and Whitney Aircraft on Several occasions between September 1978 and March 1979.

APPENDIX A

Phase Equilibria and Interstitial Effects in the Ti-V-Mo Alloy System

T. KHALED, G. H. NARAYANAN, AND S. M. COPLEY

The stability of the β phase in the Ti-V, Ti-Mo, and Ti-V-Mo alloy systems was investigated, and the $\beta/\alpha + \beta$ phase boundaries in these systems were determined in the range 300 to 600°C. The results indicate that Mo is more potent than V in stabilizing the β phase with respect to α phase formation and in retarding the $\beta - \alpha$ reaction kinetics. It is shown that increasing the oxygen concentration in the alloys tends to enhance α phase formation in Mo-lean alloys (Mo contents < 15 wt pct), whereas it leads to the formation of an oxide phase in Mo-rich alloys (Mo contents \geq 15 wt pct).

I. INTRODUCTION

THE equilibrium $\beta/\alpha + \beta$ phase boundary (β -transus) in the Ti-V-Mo system has not been, so far, experimentally determined. A number of investigators,¹⁻⁹ however, have determined the phase diagrams of the three binaries that bound the Ti-V-Mo ternary. For example, it is reported that V and Mo form a continuous series of solid solutions with one another.^{1,2} Also the Ti-V,³⁻⁶ and the Ti-Mo⁷⁻⁹ phase diagrams are reported to be of the β -isomorphous class. However, there are discrepancies between the results of different authors working on the same alloy system regarding the location of the β -transus in that system. This may be due to differences in the levels of interstitial contamination in the alloys investigated by the different authors, as is suggested in a recent theoretical calculation for the Ti-V system.¹⁰ In view of these discrepancies, it is not possible to accurately evaluate the relative β stabilizing powers of Mo and V on the basis of previous investigations.

The objective of the present work is to investigate the stability of the β phase in Ti-V, Ti-Mo and, Ti-V-Mo alloys, and the effect of oxygen on phase equilibria in the range 300 to 600°C. No attempt will be made here to compare the present results with those of previous studies concerning the Ti-V and the Ti-Mo systems because of the uncertainty in the interstitial contents of the alloys used in previous studies.

II. EXPERIMENTAL PROCEDURE

The alloys used in this work were prepared in the form of buttons from high purity metals (see Table I), by arc melting under a purified argon atmosphere, using a non-consumable tungsten electrode. All alloy buttons were melted six times and turned over prior to each remelting operation. The nominal compositions of these alloys in wt pct are shown in Table II.

All of the alloys shown in Table II, with the exception of those marked with asterisks, were cold rolled in the

as-cast condition to 0.4 mm strips, and then cut to coupons for subsequent heat treatments. The alloy compositions marked with asterisks were brittle and were not included in this work (see Ref. 11).

Two groups of alloys differing mainly in their oxygen contents were investigated. Typical interstitial analyses* of one group of alloys were 0.07 O, 0.007 N

*All analyses cited in the present work are in weight percent.

and, 0.009 C. The interstitial analyses of the other group of alloys were typically 0.12 O, 0.01 N and, 0.007 C.

Specimens for heat treatment were wrapped in Ta foils and sealed in evacuated quartz capsules. The capsules were evacuated and back-filled with purified argon several times before sealing under vacuum. A

Table I. Chemical Analyses of the Metals Used for Alloy Preparation

High Purity Crystal Bar Ti			
Element	Wt Pct		
Si	<0.005		
Al	<0.005		
Mg	<0.005		
Mn	<0.001		
Cr	<0.02		
Fe	<0.005		
Cu	<0.001		
Ni	<0.001		
Sn	<0.01		
Zr	<0.01		

High Purity V Sheet			
Element	ppm by Wt	Element	ppm by Wt
Al	50-126	Mo	<20
B	1	O	442-634
Cb	<1000	Si	<1000
Cu	<40	Ta	<50
Fe	86-92	Ti	<500
H	<5	W	100-150
Mg	33-34	C	90-130
Mn	<20	N	

Sintered Mo Bar		Wt Pct	
Element			
C			0.011
O			0.0009
H			<0.0001
N			0.0001
Fe			0.0005
Ni			<0.001

T. KHALED, formerly Research Assistant, Department of Materials Science, University of Southern California, is now Research and Development Materials Engineer, Ford Aerospace and Communications Corporation, Newport Beach, CA. G. H. NARAYANAN and S. M. COPLEY are Assistant Professor, and Professor and Chairman, respectively, Department of Materials Science, University of Southern California, Los Angeles, CA.

Manuscript submitted December 29, 1977.

recrystallization/solution heat treatment at 900°C for 3 h or 50 h was used prior to isothermal aging at lower temperatures. The variation of the recrystallized grain size with alloy composition and time is shown in Fig. 1 for both oxygen levels investigated. It can be seen from this figure that Mo is superior to V in inhibiting grain growth. To investigate phase equilibria in the range 300 to 600°C, the recrystallized/solutionized alloys were isothermally aged for 250 h at 600°C, 1500 h at 450°C, or 2000 h at 300°C.

The identification of phases present in the heat treated alloys was made primarily by transmission electron microscopy, using a Hitachi HU-125C microscope operated at 125 KV. Thin foils for microscopy work were prepared by electropolishing using the solution and conditions described by Blackburn and Williams.¹² The transmission microscopy work was supported by X-ray powder diffraction analysis using Cu-K α radiation.

In order to reveal grain boundary segregation, an Applied Research Laboratories EMX electron probe microanalyzer was used for local chemical analyses. Primary electron energies of 10 KV and 20 KV were used for interstitial (O), and substitutional (Ti, V, and Mo) elements respectively. Typical analyzed (ex-

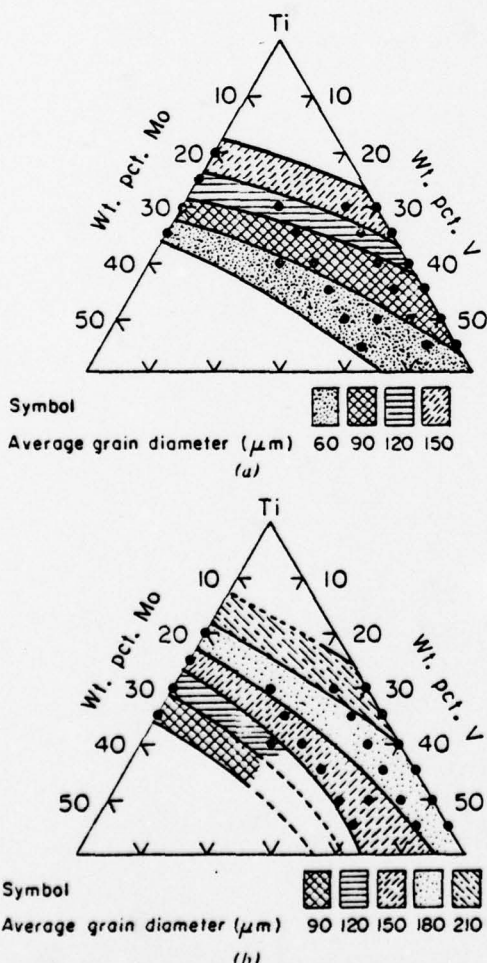


Fig. 1—Average grain diameter as a function of composition in the Ti-V-Mo system after recrystallizing at 900°C for (a) 3 h, and (b) 50 h.

Table II. Nominal Alloy Compositions

Alloy Number	Alloy Composition Wt Pct		Ti
	Mo	V	
1	—	50	50
2	—	35	65
3	—	40	60
4	—	45	55
5	—	50	50
6	—	55	45
7	5	25	70
8	5	30	65
9	5	35	60
10	5	40	55
11	5	45	50
12	5	50	45
13	10	40	50
14	15	15	70
15	15	20	65
16	15	25	60
17	15	30	55
18	15	35	50
19	15	40	45
20	20	20	60
21	20	—	80
22	25	—	75
23	30	—	70
24	35	—	65
25*	40	—	60
26*	45	—	55
27*	50	—	50
28*	55	—	45

*Brittle in the as-cast condition.

cited) volumes were 1.5 μm in diam. and 1.5 μm in depth. Grain boundary local analyses were carried out at triple points, i.e. where three grains meet, so as to maximize the grain boundary volume analyzed at any given time with respect to the volume excited by the electron beam, and consequently improving the chances of detecting grain boundary segregation.¹¹

III. EXPERIMENTAL RESULTS

A. Solution Heat Treated Microstructures

Microstructural examination of the alloys with the two investigated oxygen concentrations indicated that the only phase present in the solution heat treated condition was the β phase. Local chemical analyses did not reveal any significant segregation of Ti, V, Mo or O to the grain boundaries.

B. Phase Equilibria at 600°C

The $\beta/\alpha + \beta$ phase boundaries at this temperature for the two investigated oxygen concentrations are shown in Fig. 2. This figure clearly indicates that Mo is superior to V in stabilizing the β phase with respect to α phase formation. It is also seen that increasing the oxygen content of the alloys leads to a widening of the α/β phase field. This widening becomes less significant as the Mo content of the alloys is increased, giving rise to a $\beta/\alpha + \beta$ phase boundary that has an inverted L shape at the higher oxygen content. Figure 3 shows the effect of the oxygen content on the microstructure of a Ti-40V alloy aged at 600°C. It can be seen that the alloy exhibits

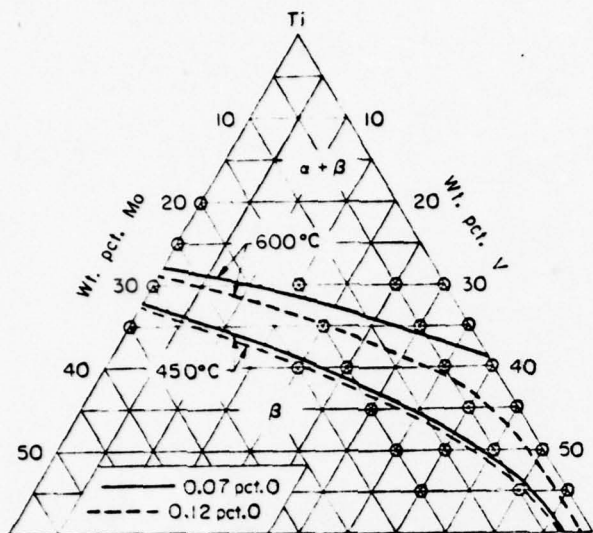


Fig. 2—The $\beta/\alpha + \beta$ phase boundaries in the Ti-V-Mo system at 600°C and 450°C for the two different oxygen concentrations.

an all β microstructure at the lower oxygen concentration (Fig. 3(a)) whereas at the higher oxygen concentration it transformed to an α/β microstructure (Fig. 3(b)).

Alloys with Mo contents ≥ 15 pct displayed a tendency towards the formation of a grain boundary phase (Fig. 4). Since this phase was not detected in Mo-free alloys, it will be referred to as the Mo-induced phase. The formation of this phase in a given alloy aged at 600°C appeared to be enhanced by coarser grain size and higher average oxygen content of the alloys. Once formed, the Mo-induced phase can be dissolved by heating at higher temperatures. The polishing and etching solutions commonly used for Ti alloys ap-

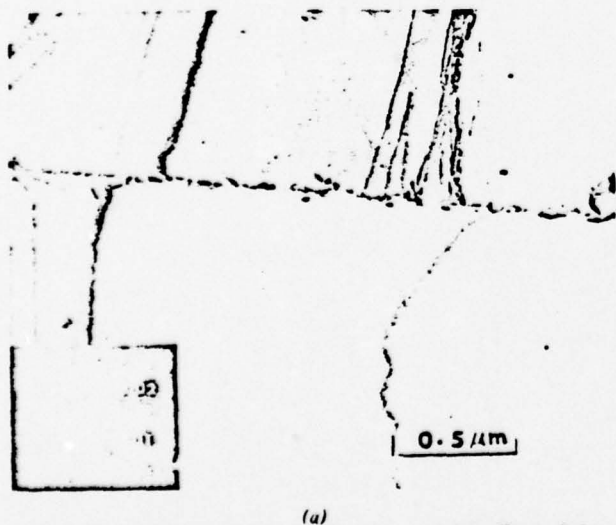
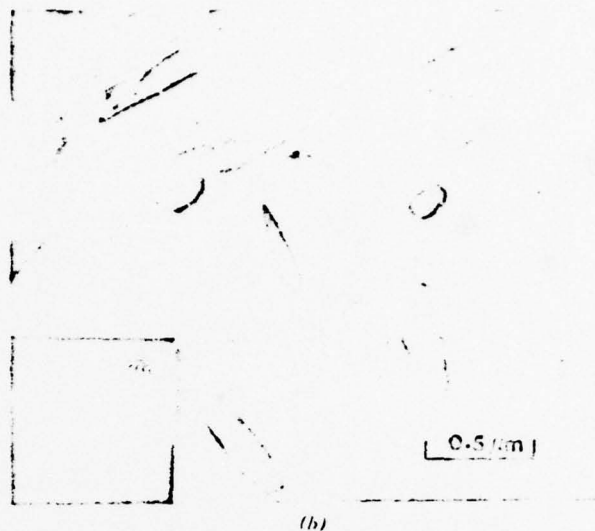


Fig. 3—B.F. electron micrographs showing the effect of the oxygen content on the microstructure of a Ti-40V alloy aged at 600°C for 250 h: (a) oxygen concentration 0.07 pct. All β microstructure with the corresponding SAD pattern. $\langle 100 \rangle \beta$ zone normal. (b) oxygen concentration 0.12 pct. α/β microstructure with the corresponding SAD pattern. $\langle 113 \rangle \beta$ and $\langle 2\bar{1}\bar{1}3 \rangle \alpha$ zone normals.



pear to preferentially attack this phase leading to its rapid dissolution. Typical electron diffraction patterns from the Mo-induced phase are shown in Fig. 5 which indicates that the crystal structure of this phase derives from a NaCl-type of structure. It was not possible, however, to obtain any new diffraction lines due to this phase in powder X-ray diffraction patterns, probably as a result of its small volume fraction, and thus its structure could not be unambiguously determined. The Mo-induced phase was detected in β and α/β alloys and its presence was associated with an intergranular brittleness.¹¹

Local chemical analyses on a number of alloys aged at 600°C revealed that Ti, V, and Mo tend to distribute themselves uniformly between the grains and the grain boundaries. In contrast, oxygen tends to segregate to the grain boundaries particularly in Mo-bearing alloys with Mo contents ≥ 15 pct. An example of this segregation is shown in Table III. For a given alloy, the concentration of segregated oxygen at the grain bound-

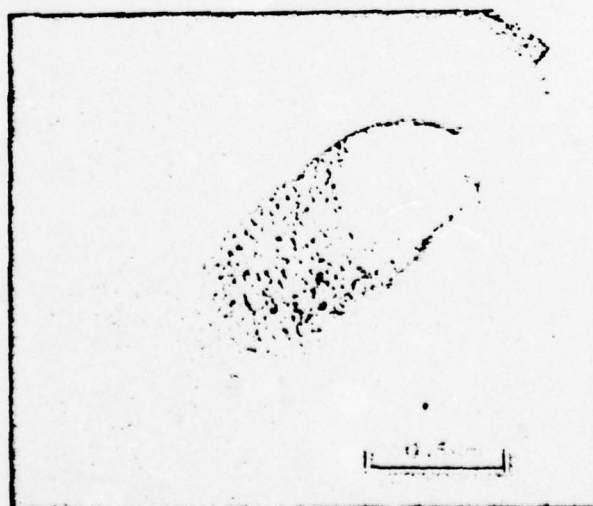


Fig. 4—B.F. electron micrograph showing the Mo-induced phase in a Ti-25V-15Mo 0.12 O alloys aged at 600°C for 250 h. Note the high density of defects and the uneven thinning of the phase.

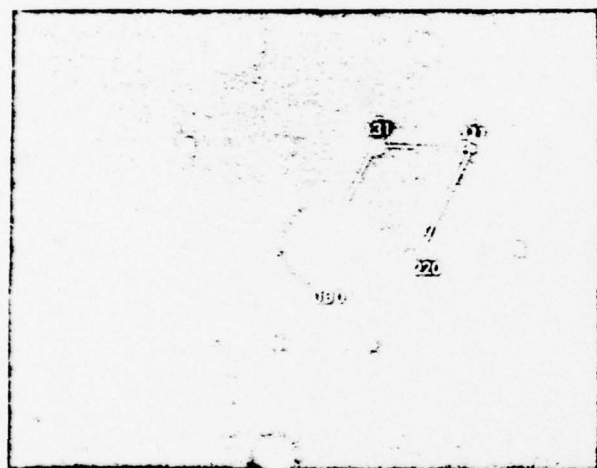
aries appeared to increase with coarser grain size and higher average oxygen content of the alloys.

C. Phase Equilibria at 450°C

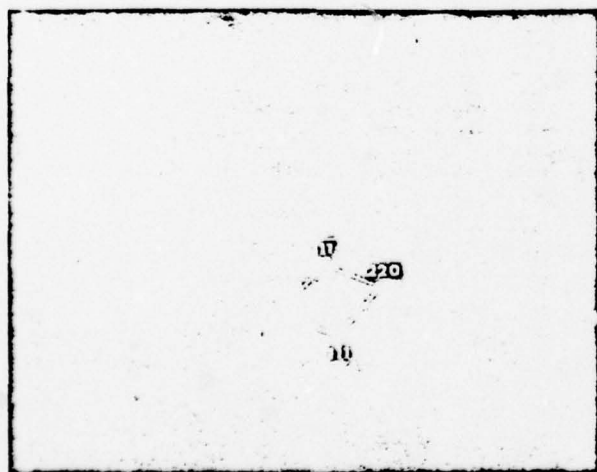
The $\beta/\alpha+\beta$ phase boundaries determined at this temperature, are shown in Fig. 2 for both oxygen concentrations investigated. These phase boundaries, in contrast to those obtained at 600°C, show that the increased presence of oxygen in the alloys at 450°C does not lead to a significant widening of the α/β phase field.

Table III. Oxygen Segregation to the Grain Boundaries in a Ti-30V-15Mo-0.12. Alloy Aged at 600°C for 250 h Average Grain Diameter 150 μm

Distance from the Grain Boundary μm	0	1	2	3	10	60
Average O counts 100 secs	192	183	146	126	128	121



(a)



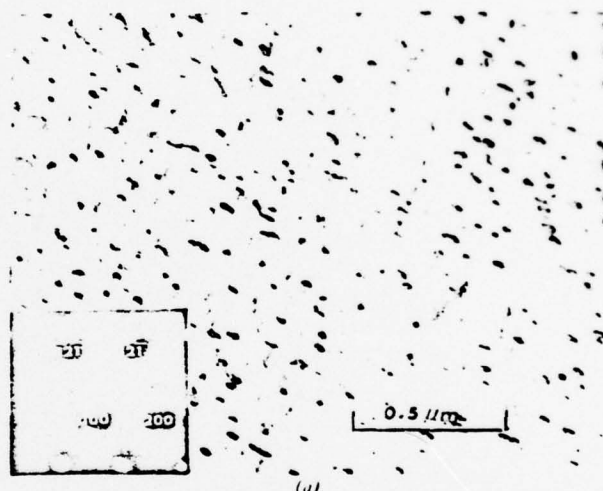
(b)

Fig. 5—SAD patterns obtained from the Mo-induced phase shown in Fig. 4 for two different foil orientations; (a) $\langle 114 \rangle$ NaCl zone normal, (b) $\langle 110 \rangle$ NaCl zone normal. Intensities of diffraction spots are modulated by the presence of extended defects within the phase.¹⁴

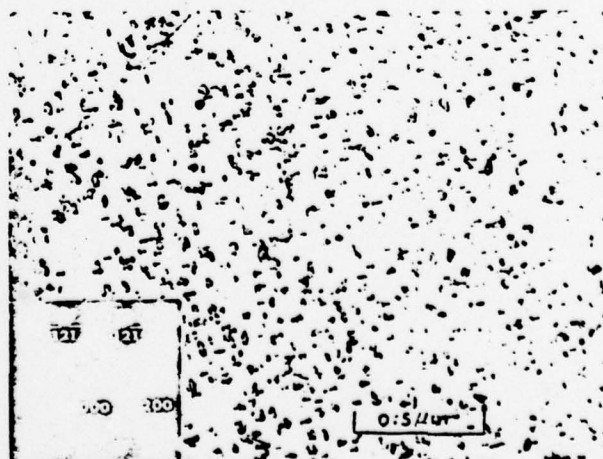
Table IV. The Effect of Mo on β/α Reaction Kinetics at 450°C

Alloy Number	Alloy Composition				Aging Times at 450°C and the Corresponding Microstructures		
	Mo	V	O	Ti	(V + Mo) pct	24 h	100 h
5	—	50	0.07	bal	50	$\beta/\alpha + \beta_1$	$\alpha + \beta$
11	5	45	0.07	bal	50	$\beta/\alpha + \beta_1$	$\beta/\alpha + \beta_1$
7	5	25	0.07	bal	30	$\beta/\alpha + \beta_1$	$\alpha + \beta$
23	30	—	0.07	bal	30	β	β

The Mo-induced phase and the tendency of oxygen to segregate to the grain boundaries were detected in alloys with Mo contents ≥ 15 pct, both being most pronounced in coarse grained alloys with the higher average oxygen concentration, as was observed at 600°C. However, for a given alloy, average oxygen concentration, and grain size, the volume fraction of the Mo-induced phase as well as the concentration of segregated oxygen at the grain boundaries were greater at 450°C than at 600°C.



(a)



(b)

Fig. 6—B.F. electron micrographs showing the β_1 precipitates formed after 24 h aging at 450°C in: (a) a Ti-30V alloy with the corresponding SAD pattern. $\langle 012 \rangle \beta$ zone normal, (b) a Ti-45V-5 Mo alloy with the corresponding SAD pattern. $\langle 012 \rangle \beta$ zone normal.

D. The Effect of Mo on the $\beta - \alpha$ Reaction Kinetics at 450°C

To determine the effect of Mo on the $\beta - \alpha$ reaction kinetics, the microstructures of those alloys with 0.07 pct O were examined as a function of aging time at 450°C. A summary of some of these results is presented in Table IV. Considering the Ti-50V and the Ti-45V-5Mo alloys, both of which containing a total of 50 pct β stabilizing elements (V and Mo), it can be seen that upon aging for 24 h at 450°C, the decomposition of the β phase in both alloys resulted in the precipitation of the solute lean β_1 phase within a solute enriched β_2 matrix (see Figs. 6(a) and (b)). However, upon aging for a total of 100 h the β_2/β_1 structure of the Ti-50V alloy transformed to an α/β structure (Fig. 7), whereas the Ti-45V-5Mo alloy remained in the β_2/β_1 condition (Fig. 8). Similarly, a comparison of the microstructure of the Ti-25V-5Mo alloy with that of the Ti-30Mo alloy in which all the V has been replaced by Mo, shows that after 100 h the former alloy developed an α/β microstructure (Fig. 9(a)) while the latter remained in the β condition (Fig. 9(b)). Since all the four alloys considered here exhibited α/β microstructures upon prolonged aging (1500 h), the preceding observations clearly demonstrate the effect of Mo in retarding the $\beta - \alpha$ reaction kinetics.

E. Phase Equilibria at 300°C

The alloys investigated at this temperature were those with 0.12 pct. average oxygen content. Figure 10 shows the phase boundaries that were determined after 2000 h of aging at 300°C. The fact that a metastable phase such as omega was detected in some alloys, suggests that the isothermal section shown in Fig. 10 is a metastable one. However, this section again demonstrates the beneficial effect of Mo additions in stabilizing the β phase. The embrittling Mo-induced phase and the tendency of oxygen to segregate to the grain boundaries were not detected in Mo-bearing alloys after aging at this temperature.

IV. DISCUSSION

A. Phase Equilibria at Low (0.07 Pct) Oxygen Contents

The shape of the phase boundaries shown in Fig. 2 (solid curves) for the alloys with low oxygen contents, indicate that Mo is a more potent β stabilizer than V. Figure 2 also shows that as the temperature is decreased from 600 to 450°C, the widening of the α/β phase field is less pronounced in Mo-rich alloys than in Mo-lean alloys. This demonstrates the better microstructural stability of Mo-rich alloys with respect to temperature changes. Thus the thermodynamic effect of Mo additions to Ti-V alloys is a widening of the β phase field at the expense of the α/β field. Apart from this effect, the results listed in Table IV indicate that the presence of Mo retards the $\beta - \alpha$ reaction kinetics in α/β alloys, as is expected from the slow diffusion rate of Mo in β Ti.¹³

B. The Origin of the Mo-Induced Phase

The present results indicate that the formation of the Mo-induced phase in Mo-bearing alloys is pro-

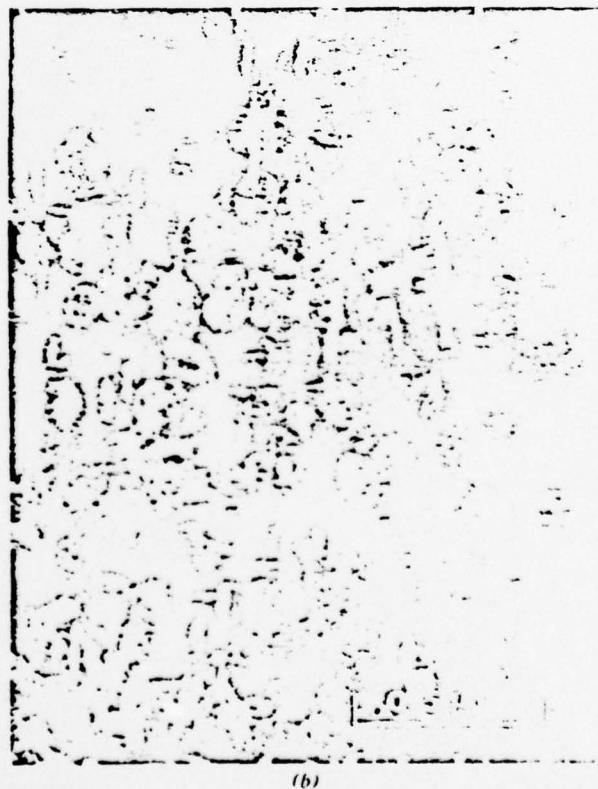
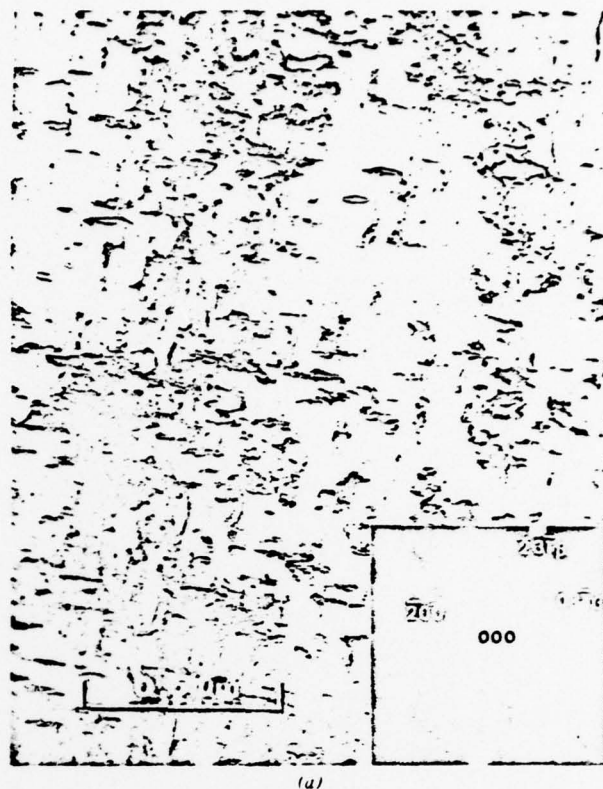


Fig. 7—Electron micrographs showing the α/β microstructure of a Ti-50V alloy aged at 450°C for 100 h. (a) B.F. with the corresponding SAD pattern. (013) β zone normal. Arcs in the diffraction spots are due to non-Burger's α . (b) D.F. obtained by using an α diffraction spot (marked α in the insert of Fig. 7(a)).

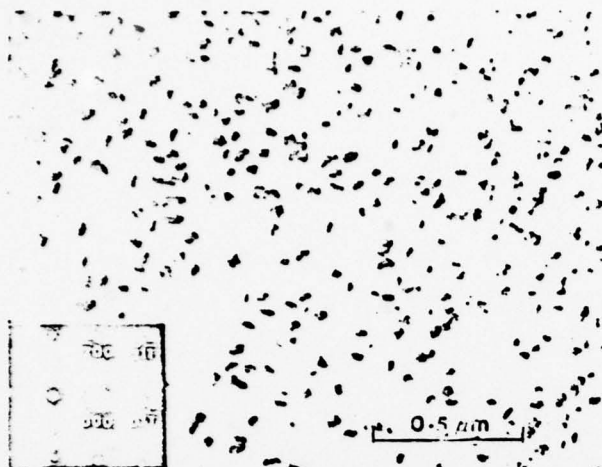
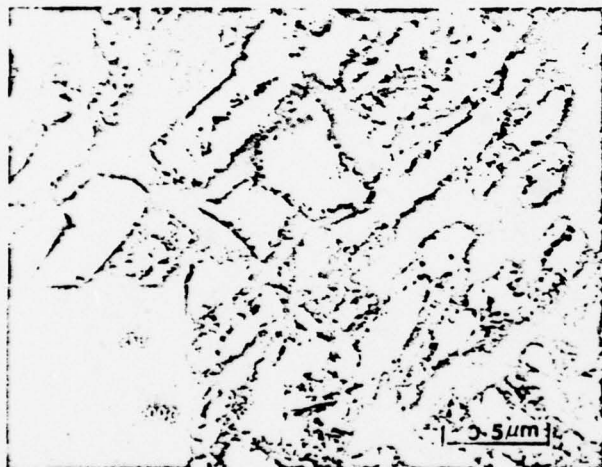
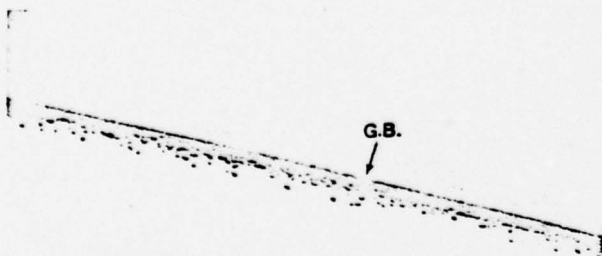


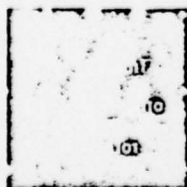
Fig. 8—B.F. electron micrograph showing the β/β_1 microstructure of a Ti-45V-5Mo alloy aged at 450°C for 100 h with the corresponding SAD pattern. $(110)\beta$ zone normal.



(a)



G.B.



(b)

Fig. 9—B.F. electron micrographs showing the microstructures obtained after 100 h aging at 450°C in: (a) a Ti-25V-5Mo alloy. α/β microstructures with the corresponding SAD pattern. $(012)\beta$ zone normal. Arcs in the diffraction spots are due to non-Burger's α . (b) a Ti-30 Mo alloy. All β microstructure with the corresponding SAD pattern. $(111)\beta$ zone normal.

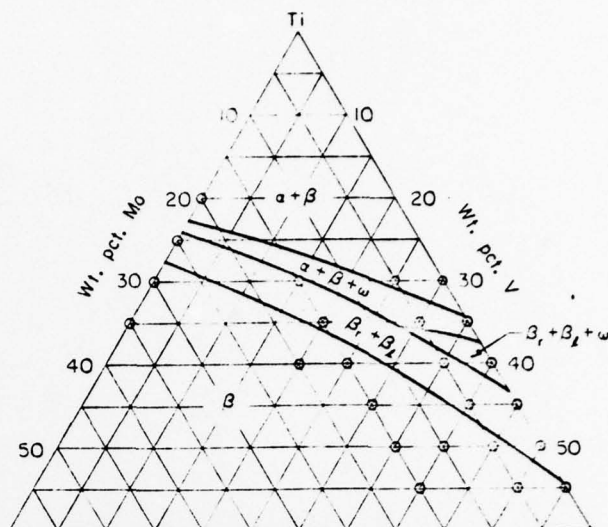


Fig. 10—Metastable phase boundaries after 2000 h aging at 300°C in alloys with 0.12 pct O.

moted by coarser grain size, higher average oxygen content, and lower aging temperatures in the range 450°C to 900°C. It is seen that these are the same factors that enhance oxygen segregation to the grain boundaries. Thus it is reasonable to assume that the Mo-induced phase is an oxide or suboxide of Ti and/or Mo. Since Ti has a higher reactivity with respect to oxygen than Mo, this phase is probably an oxide or suboxide of Ti. This conclusion is substantiated by the fact that the electron diffraction patterns obtained from the Mo-induced phase (Fig. 5) can be indexed on the basis of a NaCl type of crystal structure, as is the case with the oxides and suboxides of Ti.¹⁴ The lack of X-ray data, however, prevented a clear-cut identification of the Mo-induced phase.

The formation of the Mo-induced phase at sites such as the grain boundaries during aging can be rationalized in terms of the relative ease of nucleation and the concentration of oxygen at these sites. It is known that the critical solute (oxygen) concentration required to nucleate a precipitating phase (the Mo-induced phase) at a heterogeneity such as a grain boundary, is considerably lower than that required to initiate homogeneous nucleation within the grains. Further, it has been shown that oxygen segregates to the grain boundaries. Therefore, even when the average oxygen content of an alloy is well below that required for nucleation, owing to the preferential segregation of oxygen to the grain boundaries, the local oxygen concentration at these sites can build up to such a level as to exceed the concentration required for the heterogeneous nucleation of an oxide phase.

C. The Effect of Increasing the Oxygen Content of the Alloys On Phase Equilibria

A comparison of the results obtained at the two oxygen concentrations investigated (0.07 and 0.12 pct) indicates that increasing the oxygen content of the alloys tends to create instabilities in the β phase. These instabilities can be divided into two distinct types depending on the Mo content of the alloys:

1) Formation of Oxygen Stabilized α in Mo-Lean Alloys (Mo Contents < 15 Pct). Increasing the oxygen

content of Mo-lean alloys tends to enhance α phase formation leading to a widening of the α/β phase field at any given temperature. Figure 2 shows that this widening is more pronounced at 600°C than at 450°C. A possible explanation of this behavior can be given on the basis of free energy-composition diagrams for the α and β phases. Figure 11(a) schematically illustrates the total free energy vs composition relationships at 600°C, while Fig. 11(b) illustrates these relationships at 450°C. The β curve at 600°C is shown to have a smooth parabolic shape consistent with the experimental observation that no phase separation reaction ($\beta \rightarrow \beta_1 + \beta_2$) takes place at this temperature. At 450°C, on the other hand, the β curve is shown to be inflected, indicating the occurrence of a phase separation reaction. Also shown in Figs. 11(a) and (b) are the α phase free energy curves for the two investigated oxygen concentrations (0.07 pct and 0.12 pct). The extent of the α/β phase field at a given temperature is determined by the common tangent to the α and β free energy curves. Since oxygen is a stabilizer of the α phase, the effect of increasing its concentration in the alloys at a given temperature is to lower the α curve relative to that of the β phase, causing a shift in the tangent point on the latter curve, and a corresponding widening ($B\bar{B}$) in the α/β phase field. Decreasing the temperature from 600°C to 450°C at either oxygen concentration lowers the α curve relative to the now inflected β curve. Because of this inflection, the curvature of the β curve near the minima becomes larger than that of its counterpart at 600°C. Consequently, at 450°C, when the α curve is lowered as a result of the increased oxygen concentration, the shift ($B\bar{B}$) in the position of the tangent point on the β curve is smaller than that at 600°C. Figure 11(c) schematically depicts the resulting phase boundaries according to the preceding arguments.

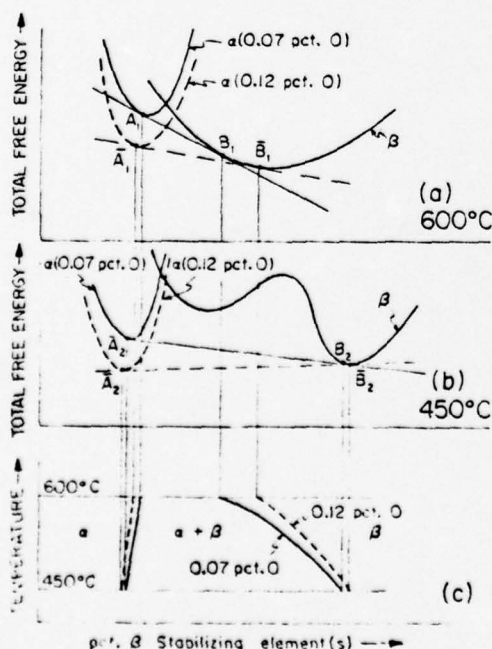


Fig. 11. Total free energy curves ((a) and (b)), and phase diagram (c) for the Ti-V-Mo system showing the effect of oxygen on phase equilibria.

2) Formation of an Embrittling Grain Boundary Oxide Phase in Mo-Rich Alloys (Mo Contents ≥ 15 Pct). The addition of about 15 pct Mo to Ti-V-alloys tends to inhibit the formation of the oxygen stabilized α phase at 600 and 450°C. These Mo-rich alloys, however, are characterized by the segregation of oxygen atoms to the grain boundaries (see Table III). This segregated oxygen tends to react with the base metals leading to the formation of the embrittling Mo-induced phase which is believed to be an oxide or sub-oxide of Ti. The formation of the Mo-induced phase was more pronounced at 450°C than at 600°C. This behavior can be rationalized in terms of a decrease in oxygen solubility in the alloys as the temperature is decreased. Such a decrease in oxygen solubility is expected to promote further segregation of this element to the grain boundaries, thus enhancing oxide phase formation. A similar tendency of carbon atoms to segregate to the grain boundaries resulting in the formation of carbides has been observed in a Ti-15 pct Mo alloy and was also attributed to solubility effects.¹⁵

The present results thus show that as the Mo content of Ti-V-Mo alloys is increased, a transition takes place in the type of instability in the β phase induced by oxygen, viz, a transition from the oxygen stabilized α phase in Mo-lean alloys to an oxide phase in Mo-rich alloys. It is interesting to note that in Zr-Nb-O alloys, a similar transition from the hcp α Zr to an oxide phase has been observed as the Nb content of the alloys is increased at a constant oxygen concentration.¹⁶ A generalized discussion of the hcp α to oxide transitions occurring in P(Ti,Zr,Hf)-X(B-stabilizer)-I(O,N,C) alloy systems is given elsewhere.¹¹

V. CONCLUSIONS

- 1) Mo is more potent than V in stabilizing the β phase.
- 2) Mo additions to Ti-V alloys retard the $\beta \rightarrow \alpha$ reaction kinetics in α/β alloys.
- 3) The increased presence of oxygen in Mo-lean alloys (Mo contents < 15 pct) enhances α phase formation and widens the α/β phase field. This widening is more pronounced at 600°C than at 450°C.
- 4) The increased presence of oxygen in Mo-rich alloys (Mo contents ≥ 15 pct) leads to the formation of an embrittling grain boundary oxide phase (the Mo-induced phase). This phase has a crystal structure that derives from a NaCl type of structure and its formation is enhanced by lower aging temperatures, higher average oxygen content, and coarser grain size.
- 5) At 300°C, the rate of attainment of equilibrium is very slow. As a result, the phase boundaries determined after 2000 h of aging at this temperature are metastable, and do not reflect the true stability of the β phase.

ACKNOWLEDGMENTS

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REFERENCES

1. J. L. Ham: *Trans. AIME*, 1951, vol. 73, p. 723.
2. W. Rostoker and A. Yamamoto: *Trans. ASM*, 1954, vol. 46, p. 1136.
3. H. K. Adenstedt, J. R. Pequinot, and J. M. Raymer: *Trans. ASM*, 1952, vol. 44, p. 990.
4. P. Pietrkowsky and P. Duwez: *Trans. AIME*, 1952, vol. 194, p. 627.
5. A. D. McQuillan: *J. Inst. Metals*, 1951-1952, vol. 80, p. 363.
6. F. Ennamis, P. A. Farrar, and H. Margolin: *Trans. TMS AIME*, 1961, vol. 221, p. 904.
7. C. M. Craighead, O. W. Simmons, and L. W. Eastwood: *Trans. AIME*, 1950, vol. 188, p. 485.
8. M. Hansen, E. L. Kamen, H. D. Keyser, and D. J. McKeown: *Trans. AIME*, 1951, vol. 191, p. 881.
9. P. Duwez: *Trans. AIME*, 1951, vol. 191, p. 765.
10. D. B. Chernov and A. Ya. Shingayev: *Russian J. Phys. Chem.*, 1975, vol. 49, no. 3, p. 445.
11. T. Kahled: Ph. D. Dissertation, University of Southern California, 1977.
12. M. J. Blackburn and J. C. Williams: *Trans. TMS AIME*, 1967, vol. 239, p. 287.
13. S. F. Fedotov, M. G. Chudinov, and K. M. Konstantinov: *Phys. Met. and Metallogr.*, 1969, vol. 27, no. 5, p. 111.
14. D. Watanabe, O. Terasaki, A. Jostsons, and J. R. Castles: *The Chemistry of Extended Defects in Non-Metallic Solids*, Leroy Eyring and Michael O'Keefe, eds., p. 238. American Elsevier, New York, 1970.
15. A. W. Bowen and C. A. Strubington: *J. Less-Common Metals*, 1970, vol. 20, no. 4, p. 367.
16. V. C. Marcotte and W. L. Larsen: *J. Less-Common Metals*, 1966, vol. 10, no. 4, p. 229.

APPENDIX B

METALLURGICAL TRANSACTIONS

Metallurgical Transactions
Carnegie-Mellon University
Schlenker Park
Pittsburgh, Pennsylvania 15213
(412) 521-2100
578-2694

January 19, 1979

Dr. Stephen Copley
Department of Materials Science
University of Southern California
Los Angeles, CA 90007

Subject: Communication (78-Comm-77-E) "Stability of the Beta Phase
in the Ti-V-Mo-Cr System" by T. Khaled, G. N. Narayanan,
and S. M. Copley

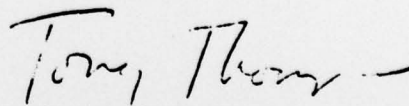
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I am pleased to report that this manuscript is recommended
for publication in METALLURGICAL TRANSACTIONS. The review committee
made constructive suggestions for clarifying its presentation, and
these are enclosed for your careful consideration. Revision, however,
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STABILITY OF THE BETA PHASE IN THE Ti-V-Mo-Cr SYSTEM

13- Comm - 11

T. Khaled, G. H. Narayanan and S. M. Copley
Department of Materials Science
University of Southern California
Los Angeles, California 90007

The authors have recently reported on phase equilibria in the Ti-V-Mo system in the temperature range 300-600°C.¹ In this communication, we report the results of an investigation of the stability of the β -phase in the Ti-V-Mo-Cr system at 400, 500 and 600°C for Cr additions up to 10 wt pct.

The compositions of the alloys investigated are given in Table I. Alloys were examined after solutionizing for 3 hours at 900°C and after subsequent aging for 250 hours at 600°C, 800 hours at 500°C or 1500 hours at 400°C. A description of the procedures employed in melting, heat treating and characterizing the alloys has been given elsewhere.^{1,2}

Microstructural examination of all alloys after solutionizing at 900°C indicated that only the beta phase was present. Local chemical analysis using an electron probe microanalyzer revealed no significant Ti, V, Mo, Cr or O segregation to the grain boundaries. A systematic investigation of the microstructures of aged alloys was carried out primarily on those containing 8 wt pct Cr. In addition, the microstructures of selected alloys containing 5 and 10 wt pct Cr were investigated.

The $\beta/(\alpha + \beta)$ phase boundary for Ti-V-Mo-8 wt pct Cr alloys at 600°C is shown in Fig. 1 (solid line). As was previously observed in Ti-V-Mo alloys, Mo is more potent than V in stabilizing the β phase with respect to α phase formation.¹ Also, as was previously observed in Ti-V-Mo alloys containing 1200ppm O, the $\alpha + \beta$ phase field widens appreciably with decreasing

Mo content giving it an inverted L shape. Alloys with Mo content < 7 wt pct and with compositions lying below line AB (i.e. those compositions lying in the shaded region of the diagram) had grain boundaries that were decorated with α phase precipitates; however, no α phase was observed in the grain interiors, after 250 hrs. of aging, see Fig. 2a. This behavior differs from that observed in Ti-V-Mo alloys with low Mo content, which contained 1200 ppm O, where α phase normally appeared both at the grain boundaries and interiors.¹ Alloys with Mo content ≥ 10 wt pct and with compositions lying below line AB had grain boundaries that were decorated only by a phase having a crystal structure that derives from NaCl-type of structure. This phase, identified previously as the Mo-induced phase (MIP), has been observed in Ti-V-Mo alloys and is believed to be an oxide or suboxide of Ti.¹ In alloys with 7 wt pct Mo content and with compositions lying below line AB, some grain boundaries were decorated by the α phase and some by the MIP. Thus, as the Mo content is increased a transition in the type of grain boundary phase is observed.

Electron probe microanalysis of several aged alloys indicated that Ti, V, Mo and Cr. were uniformly distributed but that oxygen has segregated to the grain boundaries. This segregation was most pronounced in coarse grained alloys with high Mo content, as was observed in Ti-Mo-V alloys.¹

The details of phase equilibria and segregation trends after aging for 800 hours at 500°C were essentially the same as at 600°C and the phase boundary at 600°C , Fig. 1, can be employed to describe the $\beta/(\alpha+\beta)$ equilibrium also at 500°C . The Ti-44V-8Cr alloy was exceptional, however, in that it exhibited a β_r (solute rich β)/ β_l (solute lean β) phase structure within the grains even after 800 hrs. of aging at 500°C . In contrast to all other alloys in the shaded region of the diagram in Fig. 1, this

alloy had α phase on just a few rather than all of the grain boundaries examined.

Aging at 400°C for 1500 hours resulted in the decomposition of the β phase in all of the alloys investigated. Some of the alloys contained β_r and β_l , while the others had α/β microstructures. The $(\beta_r + \beta_l)/(\alpha + \beta)$ phase boundary is shown in Fig. 3. Alloys with $\beta_r + \beta_l$ microstructures characteristically lacked grain boundary phases.

Only a few alloys with 5 and 10 wt pct Cr were investigated. The microstructures of these alloys after aging at 400, 500 and 600°C are described in Table II. As in the case of the 8% Cr alloys with compositions lying below line AB, aging at 500 or 600°C resulted in the formation of the α phase at the grain boundaries of Mo lean alloys and the formation of the MIP at the grain boundaries of Mo rich alloys; in both cases, the grain interiors were β phase. A deviation from this behavior was observed in the Ti-30V-5Mo-10Cr alloy aged at 500°C. This alloy had a $\beta_r + \beta_l$ microstructure throughout and α phase was not detected at the grain boundaries examined. Aging at 400°C resulted in the formation of a $\beta_r + \beta_l$ microstructure in all of the alloys with no grain boundary phases being present.

The similarity of the inverted L shaped $(\alpha+\beta)/\beta$ boundary observed in Ti-V-Mo-8Cr system to that observed in the Ti-V-Mo system with 1200 ppm oxygen suggests that phase equilibria observed in the present investigation were probably influenced by the presence of oxygen. In both systems, the results indicate that in oxygen bearing alloys, as the Mo content of the alloy is increased, there is a transition in the type of grain boundary phase present; namely, the α phase occurs in Mo-lean alloys while, the MIP occurs in Mo-rich alloys. The nature of this influence can be qualitatively understood with the help of the schematic Ti-X-O diagram shown in Fig. 4 which is based on the Ti-Mo-O diagram determined by Farrar et al.³

According to this diagram, if oxygen is present in excess of its solubility limit in the β phase, then as was observed, a transition in the oxygen stabilized phase will occur with increasing fraction of β stabilizers viz. $\alpha + \beta \rightarrow \alpha + \beta + (Ti,X)O \rightarrow \beta + (Ti,X)O$, see arrow in Fig. 4. Since it has been shown that Mo is the most potent of all the alloying elements in the Ti-V-Mo-Cr system in stabilizing the β phase², increasing the proportion of Mo with respect to V at constant amount of alloying addition, in effect, also shifts the phase equilibria in the direction of the arrow shown. Because of the influence of oxygen on phase equilibria, no attempt will be made to compare the results of the present investigation with the results of others on related ternary systems where the interstitial content was not reported.⁴⁻⁶

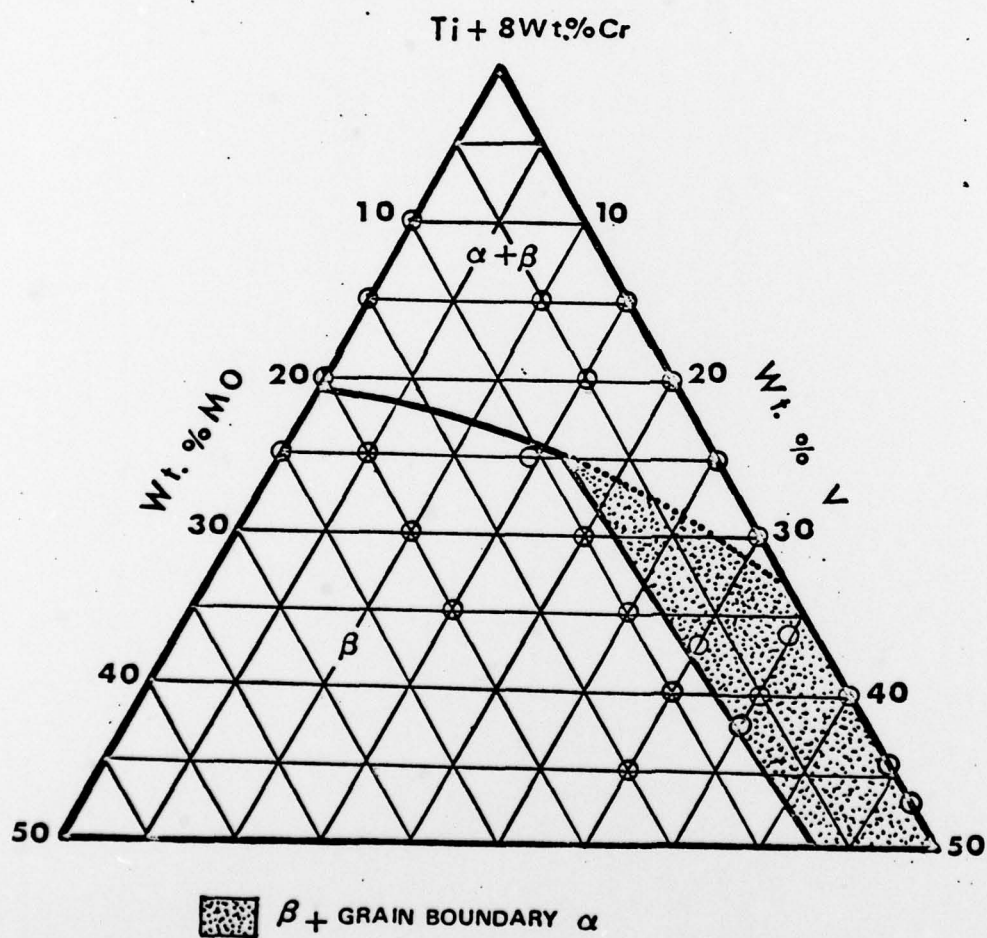
The observation that α precipitated both at grain boundaries and at grain interiors in the Ti-V-Mo alloys, but only at grain boundaries in many of the Ti-V-Mo-8Cr alloys having comparable amounts of beta stabilizing elements is attributed to the lower concentrations of oxygen and/or the greater stability of the β phase in the latter alloys. The total absence of α from the grain boundaries of alloys aged at 400°C may be due to low oxygen diffusivity at this temperature.

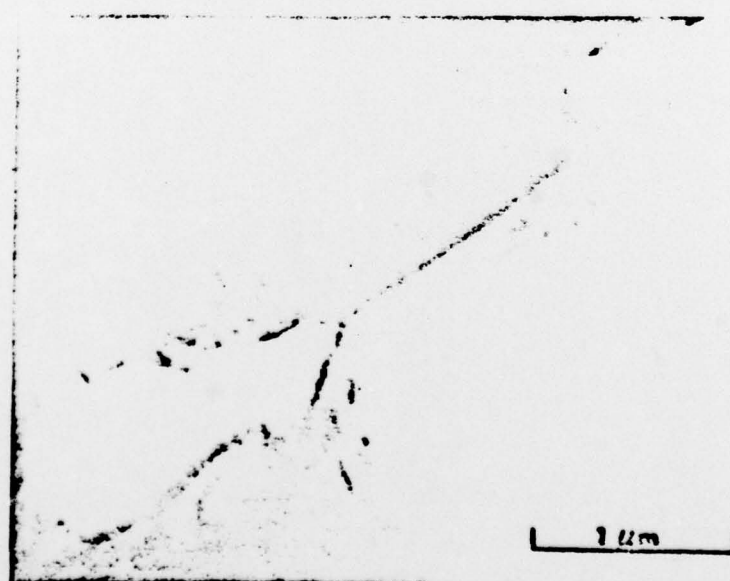
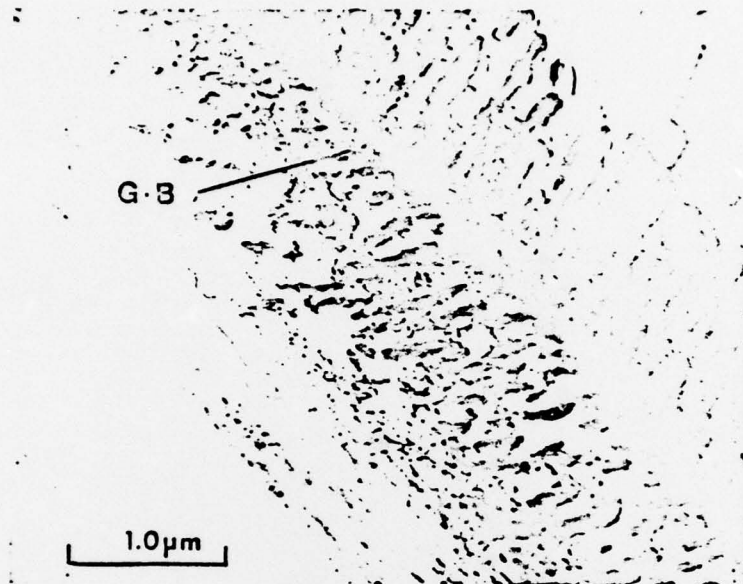
The apparent stability of the $\beta_r + \beta_l$ microstructure in alloys 6 and 32 at 500°C has led to a speculation about the possibility of a stable miscibility gap,² similar to that reported in the Ti-W system⁷. The observation of $\alpha + \beta$ microstructures in these alloys at 600°C would, however, appear to rule out this possibility.

REFERENCES

1. T. Khaled, G. H. Narayanan and S. M. Copley: Met. Trans., 1978, Vol. 9, p. 111.
2. T. Khaled: Ph.D. Dissertation, University of Southern California, 1977.
3. P. A. Farrar, K. P. Stone and H. Margolin: J. Met., 1956, vol. 8, p. 595.
4. P. A. Farrar and H. Margolin: ASM Trans. Quart., 1967, vol. 60, p. 57.
5. R. P. Elliot, B. W. Levinger and W. Rostoker: J. Met., 1953, vol. 5, p. 1544.
6. H. R. Ogden, F. C. Holden and R. I. Jaffee: A Symposium on Titanium, p. 32, ASTM, 1957.
7. E. Rudy and St. Windisch: Trans. AIME, 1978, vol. 242, p. 953.

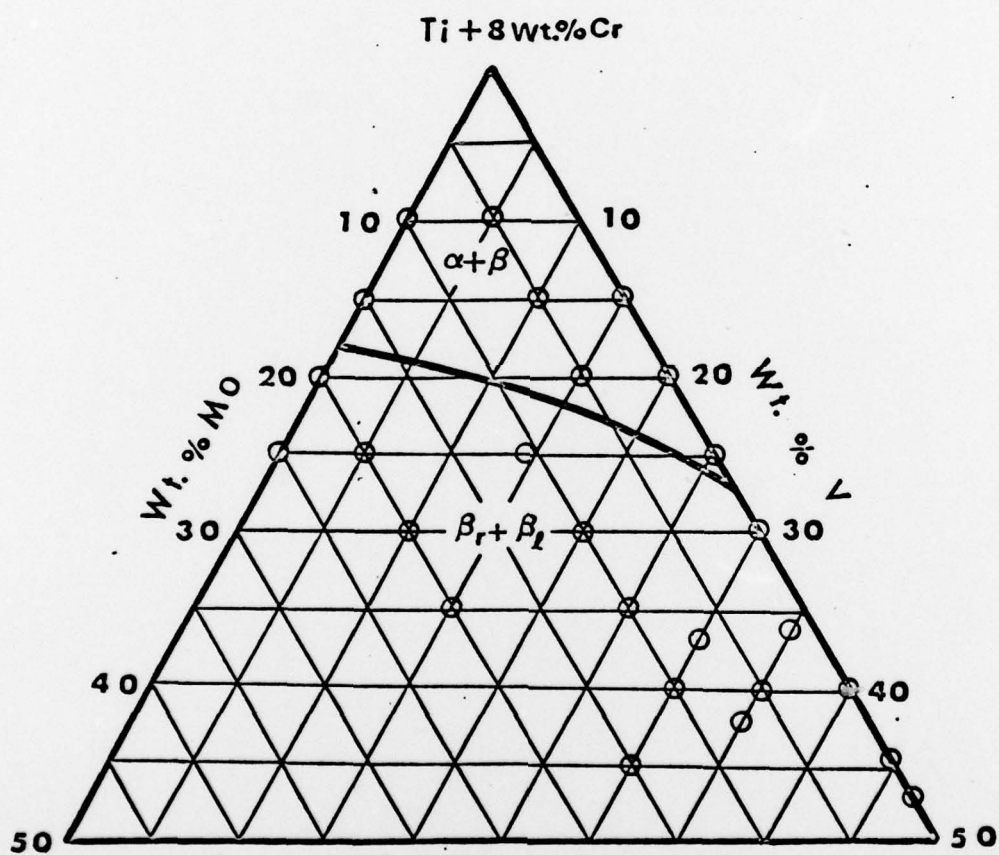
(Fig 1)

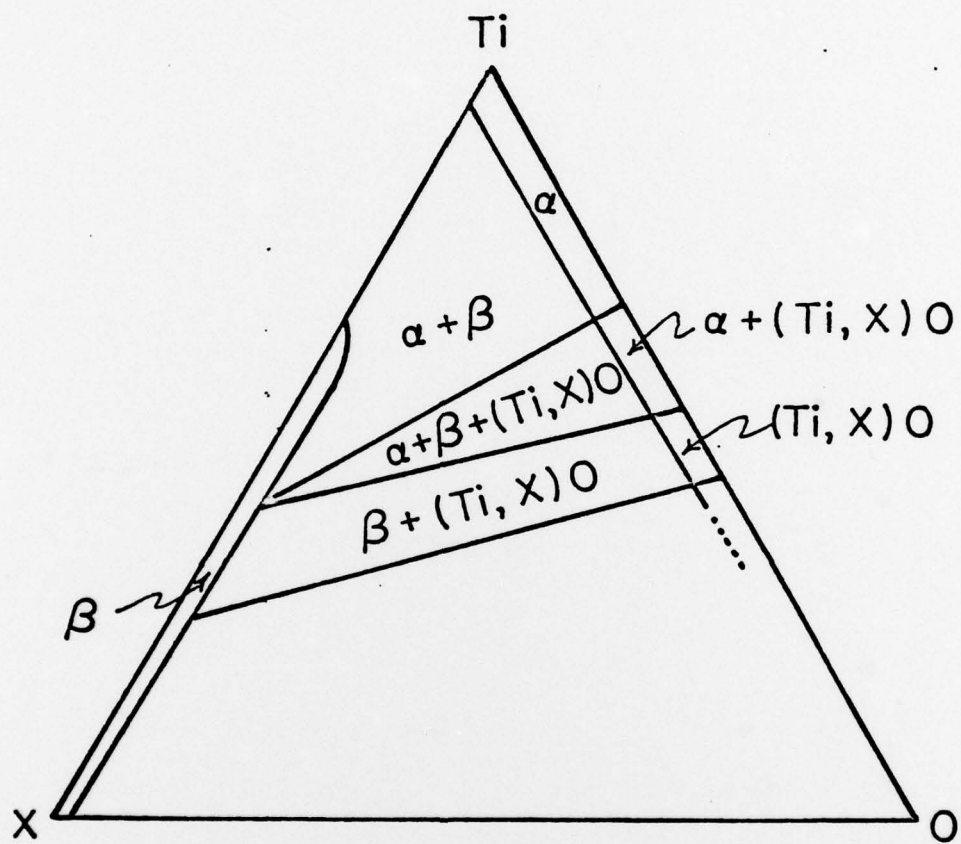




200

Fig 3





Alloy

Composition (wt pct)

	<u>Ti</u>	<u>V</u>	<u>Mo</u>	<u>Cr</u>
1	77	15	-	8
2	72	20	-	8
3	67	25	-	8
4	62	30	-	8
5	52	40	-	8
6	48	44	-	8
7	45	47	-	8
8	55	35	2	8
9	77	10	5	8
10	72	15	5	8
11	52	35	5	8
12	55	30	7	8
13	50	35	7	8
14	82	-	10	8
15	67	15	10	8
16	62	20	10	8
17	57	25	10	8
18	52	30	10	8
19	77	-	15	8
20	47	30	15	8
21	72	-	20	8
22	67	5	20	8
23	62	10	20	8
24	57	15	20	8
25	67	-	25	8
26	50	45	-	5
27	45	50	-	5

Alloy	Composition (wt pct)			
	<u>Ti</u>	<u>V</u>	<u>Mo</u>	<u>Cr</u>
28	55	30	10	5
29	50	35	10	5
30	45	35	15	5
31	45	45	-	10
32	55	30	5	10

Table I

Compositions of the alloys investigated. Chemical analysis indicated that alloys contained 900 ppm oxygen, 100 ppm nitrogen and 80 ppm carbon.

Table II

Microstructures of the investigated alloys in the 5 and 10
wt% Cr sections of the Ti-V-Mo-Cr quaternary

Alloy #	Aging temps. and microstructures [†]		
	600 ° C	500 ° C	400 ° C
26	$\alpha_{G.b} + \beta$	$\alpha_{G.b} + \beta$	$\beta_r + \beta_L$
27	$\alpha_{G.b} + \beta$	$\alpha_{G.b} + \beta$	$\beta_r + \beta_L$
28	$\beta + MIP$	$\beta + MIP$	$\beta_r + \beta_L$
29	$\beta + MIP$	$\beta + MIP$	$\beta_r + \beta_L$
30	$\beta + MIP$	$\beta + MIP$	$\beta_r + \beta_L$
31	$\alpha_{G.b} + \beta$	$\alpha_{G.b} + \beta$	$\beta_r + \beta_L$
32	$\alpha_{G.b} + \beta$	$\beta_r + \beta_L$	$\beta_r + \beta_L$

[†]G.b = grain boundaries.

FIGURES

- Figure 1: The $(\alpha+\beta)/\beta$ phase boundary in the Ti-V-Mo-8Cr system at 500 and 600° C.
- Figure 2: Grain boundary phases in Ti-V-Mo-8Cr alloys: (a) α phase in a Ti-47V-8Cr alloy aged at 600° C for 250 hours (Insert shows the corresponding S.A.D. pattern, $\langle 111 \rangle \beta$ zone normal); (b) MIP phase in Ti-35V-7Mo-8Cr alloy aged at 500° C for 800 hours.
- Figure 3: The $(\beta_r + \beta_l)/(\alpha+\beta)$ phase boundary in the Ti-V-Mo-8Cr system at 400° C (aging time 1500 hours).
- Figure 4: Schematic Ti-X-0 diagram.